

Organic Matter in Fresh Waters of South Florida

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THE relative abundance of organic matter is of considerable importance in delimiting the level of productivity in an aquatic ecosystem (Reid, 1967), but accurate measurement of organic matter in water is often difficult because of the varying physical states and amounts of organic and inorganic substances. Organic matter is present in solution in fresh water, as organic debris, and as plankton. It is derived from allochthonous material carried into the water from outside sources, and from autochthonous matter produced within the body of water by living organisms.

The ashing method is the most common means of measuring total organic matter. This is accomplished by determining the loss of weight on ignition of a sample that has been evaporated to dryness (Hutchinson, 1957). This procedure gives an ash free dry weight which is only an indirect estimate of the organic matter because it carries an error proportional to the amount of volatile inorganic material present (American Public Health Association, 1965).

A number of hydrochemical methods of organic matter analyses, using dichromate oxidation, have been described in recent years by Moore, et al. (1949), Moore and Walker (1956), Nikolaeva (1953), Votintsev (1955), and Maciolek (1962). Maciolek's method was designed to measure the very small quantities of organic matter found in mountain lakes of western United States.

In our work we have found the ashing method generally unsatisfactory; therefore, the purpose of this study was to determine if Maciolek's method could be applied satisfactorily to the diverse limnological conditions, and to the large quantities of organic matter, found in the fresh waters of southern Florida. Measurements of organic matter by ashing and pilot analyses by dichromate oxidation showed that the quantity of total organic matter usually exceeded 10 mg per liter and some waters contained more than 100 mg per liter. These amounts far exceed those reported for other waters in the United States. Maciolek (1962, 1968) reported that the waters of high mountain lakes contained 1.05-1.84 mg per liter of organic matter. The lakes of Wisconsin were reported by Birge and Juday (1934) to have an organic content of 3.71-50.34

mg per liter. Applegate and Mullan (1967) found the fresh water reservoirs in Arkansas to contain 6.87-7.42 mg per liter of organic matter.

To ascertain the range in amounts of organic matter, locations were selected to provide samples from a variety of aquatic environments, as follows: Station 1, Deep Lake, Collier County, Township 51 S, Range 30 E, Section 7; Station 2, Tamiami Trail Canal, Collier County, T. 53 S, R. 32 E, Sec. 12; Station 3, Tamiami Trail Canal, Collier County, T. 53 S, R. 30 E, Sec. 18; Station 4, Tamiami Trail Canal, Dade County, T. 54 S, R. 39 E, Sec. 6; Station 5, Survey Pond (a quarry pond), Dade County, T. 54 S, R. 39 E, Sec. 6; Station 6, Redskin Pond (a quarry pond), T. 54 S, R. 39 E, Sec. 3; Station 7, Coral Park Lake (a quarry lake), Dade County, T. 54 S, R. 39 E, Sec. 8; Station 8, Lake Catalina (a quarry lake), Dade County, T. 54 S, R. 40 E, Sec. 22; Station 9, Rockpit No. 1 (a quarry pond), Dade County, T. 54 S, R. 40 E, Sec. 22; Station 10, Cypress strand, Monroe County, T. 54 S, R. 33 E; Station 11, Rockpit No. 2 (a quarry pond), Dade County, T. 54 S, R. 40 E, Sec. 22; Station 12, Coral Lake (a quarry lake), Dade County, T. 54 S, R. 40 E, Sec. 23; Station 13, Coral Gables Canal, Dade County, T. 53 S, R. 40 E, Sec. 13; Station 14, Lake Okeechobee, South Bay, Palm Beach County, T. 43 S, R. 36 E; Station 15, Black Creek, Dade County, T. 55 S, R. 40 E, Sec. 32; Station 16, Rockpit No. 3 (a quarry pond), Broward County, T. 50 S, R. 39 E, Sec. 10; Station 17, Rockpit No. 4 (a quarry pond), Dade County, T. 56 S, R. 40 E, Sec. 4; Station 18, Snapper Creek, Dade County, T. 54 S, R. 40 E, Sec. 35; Station 19, Cattail Pond, Dade County, T. 53 S, R. 40 E, Sec. 32; Station 20, Kendall Lake (a quarry lake), Dade County, T. 55 S, R. 40 E, Sec. 10; Station 21, Conservation Area No. 3, Everglades, Dade County, T. 54 S, R. 38 E, Sec. 4; Station 22, Airport Rockpit (a quarry pond), Dade County, T. 54 S, R. 40 E, Sec. 1; Station 23, Miller Lake, (a quarry lake), Dade County, T. 54 S, R. 40 E, Sec. 23; Station 24, Conservation Area No. 2, Everglades, Broward County, T. 49 S, R. 39 E, Sec. 15.

METHODS

Our procedure generally followed the micro method of Maciolek (1962). Three 100 ml samples of water were taken at each station and evaporated to dryness at 95 C. A measured volume of potassium dichromate solution and twice as much concentrated sulphuric acid were added to the samples which were then placed in a boiling water bath for 3 hours. After cooling, the reaction mixture was diluted with distilled water and the excess dichromate titrated with a solution of ferrous sulphate, using barium diphenylamine sulfonate as the indicator. The end point is very sharp; the color of the solution changing from a reddish blue to bright green.

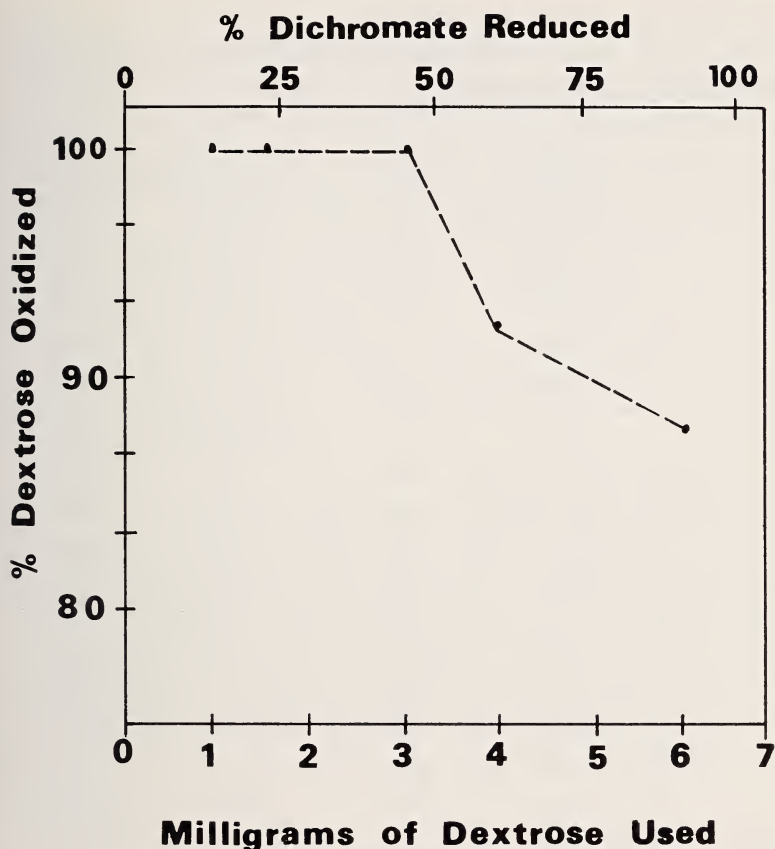


Fig. 1. Comparison of the amount of dextrose oxidized and the amount of 5 ml of 0.20 N dichromate reduced.

We find that the ferrous sulphate solution should be standardized daily because of its tendency towards autodecomposition.

In employing this method (Maciolek, 1962) the oxygen consumed (O.C.) values are derived from the difference between the sample and reagent blank titres. The total organic matter in mg per liter is obtained by multiplying the O.C. values of the samples by the reciprocal of 1.43 (= 0.7). This universal factor was based on analysis of a great many representative substrates. In using this constant, the calculated organic weight is expected to be ± 10 per cent of the true value. The O.C. value (in mg) is converted into

TABLE 1

The percentage of 0.200N potassium dichromate reduced and total organic matter present in a number of South Florida waters

Station*	Date Collected 1968	Organic matter mg/l	Percentage of dichromate reduced	Standard deviation
1	6/29	36.0	60.0	0.046
2	6/29	19.1	31.9	0.000
3	6/29	29.1	52.5	0.058
4	6/29	36.4	64.0	0.095
5	6/29	43.2	82.0	0.200
6	6/29	36.9	46.5	0.116
7	6/29	22.4	39.3	0.050
8	6/29	12.0	21.6	0.000
9	6/29	15.2	27.3	0.090
10	6/29	19.6	33.7	0.117
11	6/29	10.8	17.4	0.000
12	6/21	14.8	26.8	0.046
13	6/25	17.4	31.4	0.612
14	4/27	43.0	81.9	0.000
23	6/27	11.1	19.4	0.108

*Three 100 ml samples of surface water were processed for each station.

organic energy in gram calories by multiplying it by 3.4. Organic carbon in the sample is calculated by multiplying the O.C. value by the reciprocal of 2.86 ($=0.35$).

To determine whether one normality of potassium dichromate would be sensitive to, and measure accurately, very small as well as large quantities of organic matter and still give acceptable results, a large number of waters were sampled using replicate 100 ml samples. These were analyzed using different volumes of potassium dichromate and normalities which ranged from 0.05-

2.00. The results indicated that 5 ml of a 0.200 N solution gave satisfactory measurements of organic matter.

To further determine if this one normality would best apply to a variety of conditions, 5 ml of 0.200 N dichromate solution was tested on precisely weighed amounts of dextrose, ranging from 0.6 mg-6 mg, in order to determine the effectiveness and sensitivity of this solution. Fig. 1 shows that up to 3 mg of dextrose was oxidized to 96 per cent by this normality with about 50 per cent of the dichromate being reduced, a condition which Maciolek (1962) indicates gives the best analytical result. The 3.0 mg of dextrose is the equivalent of 30 mg of organic matter per liter of water when a 100 ml sample is processed. Fig. 1 also indicates that amounts of dextrose as small as 0.6 mg (=6 mg of organic matter per liter) can be measured accurately.

The data in Fig. 1 can be used to adjust the sample size, the normality, or the volume of dichromate to obtain the highest degree of accuracy. Table 1 indicates that 0.200 N dichromate is satisfactory for measuring the organic matter in a variety of conditions. In this series of pilot analyses, the per cent of dichromate reduced varied from 17.4-82.0 when the weight of organic matter varied from 10.8-43.2 mg per liter. These data also show that with good analytical methods a single normality can be used and still maintain a very low standard deviation when replicate samples are processed. This was not the case when other normalities of dichromate were tested.

To compare the dichromate and the ashing methods, a number of duplicate 100 ml water samples were dried at 103 C, weighed, ignited at 600 C for 1 hour in a muffle furnace, and reweighed. The samples were then hydrated with a few drops of distilled water which had a high CO_2 content and allowed to sit for 4 hours. They were then dried at 103 C and weighed again. This gave the ash free dry weight after hydration which was compared to results obtained by processing duplicate samples by dichromate oxidation.

To determine the affects of volatile inorganic matter on the ashing method, duplicate 100 mg samples of anhydrous calcium bicarbonate were ignited at 600 C for 1 hour. This resulted in all but 2 mg of the calcium bicarbonate being burned off. The samples were hydrated and dried, with the total weight of the

calcium bicarbonate being regained. This was not the case when the same amount of sodium bicarbonate was treated in the same manner, since 60 per cent of it was lost on ignition with no weight being regained by the sample after hydration.

A number of methods were employed to determine the size of the particles of the organic matter in local waters. Apparatus used was the Foerst plankton centrifuge, no. 50 Whatman filter paper, and Milipore filters ranging from 5μ - 0.22μ in pore size. The 0.45μ Milipore filter removed all living organisms and everything passing through was considered to be in a dissolved state.

COMPARISON OF ASHING AND DICHROMATE METHODS

Samples from 22 stations were analysed by the two methods. The results showed a general lack of agreement in the amount of organic matter present at 20 stations (Table 2). In only two cases (Stations 15 and 17) were the quantities of organic matter, as measured by the two procedures, virtually identical. It is apparent from the data that in most cases the amount of organic matter, expressed as hydrated ash free dry weight (AFWH), was greater than the amounts measured by dichromate oxidation (DM). However, in 25 per cent of the samples compared the reverse was true. The greatest discrepancies were encountered at stations 11, 13, and 22, where the percentage of difference was 101, 106, and 138, respectively.

Non-hydrated ashed samples (AFW) from all 22 stations had results that were generally much higher when compared with duplicate samples processed using the dichromate method. The difference varied from 5.3-353 per cent, and the average variation, when all 22 stations were compared, was 109 per cent.

In evaluating the ashing method the data in Table 2 shows that in all but 4 cases (stations 4, 9, 10, and 23) the non-hydrated ash gave a weight loss on ignition greater than duplicate samples that were processed by hydrating the ash. Two stations (4 and 23) showed identical results. The data from stations 9 and 10 were contrary to expected results, since it showed an increase in the hydrated ash free dry weight.

Total alkalinity was measured at several stations and the data compared to the difference between the hydrated and non-hydrated ash free dry weight of samples taken from the same station.

TABLE 2

Comparison of total organic matter measured by ashing and dichromate methods

Station	Date 1968	DW*	AFW	AFWH	DM
1	6/29	208	48	41	36.0
2	6/29	179	35	31	18.5
3	6/29	223	45	34	29.1
4	6/29	241	39	39	36.4
5	6/29	327	84	50	43.2
6	6/29	254	54	44	36.9
7	6/29	300	80	29	22.4
8	6/29	207	35	7	12.0
9	6/29	165	16	25	15.2
10	6/29	173	31	36	19.6
11	6/29	242	42	5	10.1
13	8/09	386	147	71	34.4
14	7/28	681	159	102	108.8
15	8/17	258	14	6	6.1
16	8/10	451	105	37	54.0
17	8/17	153	34	23	22.9
18	8/17	300	39	23	31.8
19	7/27	331	53	43	26.8
20	8/03	187	27	12	10.4
21	8/04	160	30	24	21.3
22	8/10	214	82	65	27.2
23	6/27	231	14	14	11.1

*Weights are in mg per liter and are the mean of 3 samples of unfiltered surface water. DW = Dry Weight; AFW = Ash-Free Dry Weight; AFWH = Hydrated Ash-Free Dry Weight; DM = Dichromate Method.

There is some indication that the degree of discrepancy between the non-hydrated and hydrated samples is related to the quantity of alkaline substances present. Of the stations sampled, those that had the higher total alkalinity had the highest percentage of difference, with the reverse being true for the stations with low alkalinity.

Both methods were again compared using dried periphyton. The periphyton communities which consist mainly of blue-green algae precipitate large quantities of calcium carbonate and have an organic content, measured by ashing, ranging from 99 to 27 per cent depending on the age of the community (Van Meter, 1965). Because of the large quantities of carbonate in some of these samples we were in doubt as to the accuracy of this method, especially when the ash was not hydrated. We processed several samples of periphyton from Station 19 and found an average organic content of 26.0 per cent using the ashing method and 26.4 per cent using the dichromate method. Samples from Station 21 had an organic content of 88.0 per cent measured by ashing and 85.5 per cent employing dichromate. These comparative results are very close and indicate that the ashing technique works well when the inorganic matter present is chiefly calcium carbonate.

Plankton samples from Coral Gables Canal (Station 13) were obtained by passing water through a Foerst plankton centrifuge at a rate of 1 liter of water in 6 minutes. The plankton concentrate was dried at 95 C and three replicate samples were processed by both methods. The ashing procedure gave a mean organic content of 1.60 mg per liter, while the dichromate method showed a mean organic content of 1.63 mg per liter. This comparison also showed good agreement between the two methods when the organic matter is free of contamination by large quantities of volatile inorganic substances.

While the ashing method appeared to give accurate results when the material tested consisted essentially of organic matter such as plankton or periphyton, it was much less reliable when applied to a variety of water samples. The dichromate oxidation procedure is clearly superior for the analysis of a large variety of aquatic samples wherein the kinds and amounts of organic and inorganic substances vary greatly.

VERTICAL DISTRIBUTION OF ORGANIC MATTER IN DEEP LAKE

Deep Lake (Station 1) was selected to study the vertical variations of organic matter in a deep water environment. It is a sink-hole that has an area of 1.52 acres and a depth of 95 feet (Parker and Cooke, 1944). The upper limits of a persistent chemocline is located at a depth of about 75 feet (Hunt, 1958). Our data show that the amount of organic matter rises sharply below 75 feet (Fig. 2), with the maximum measured amount being 110.5 mg

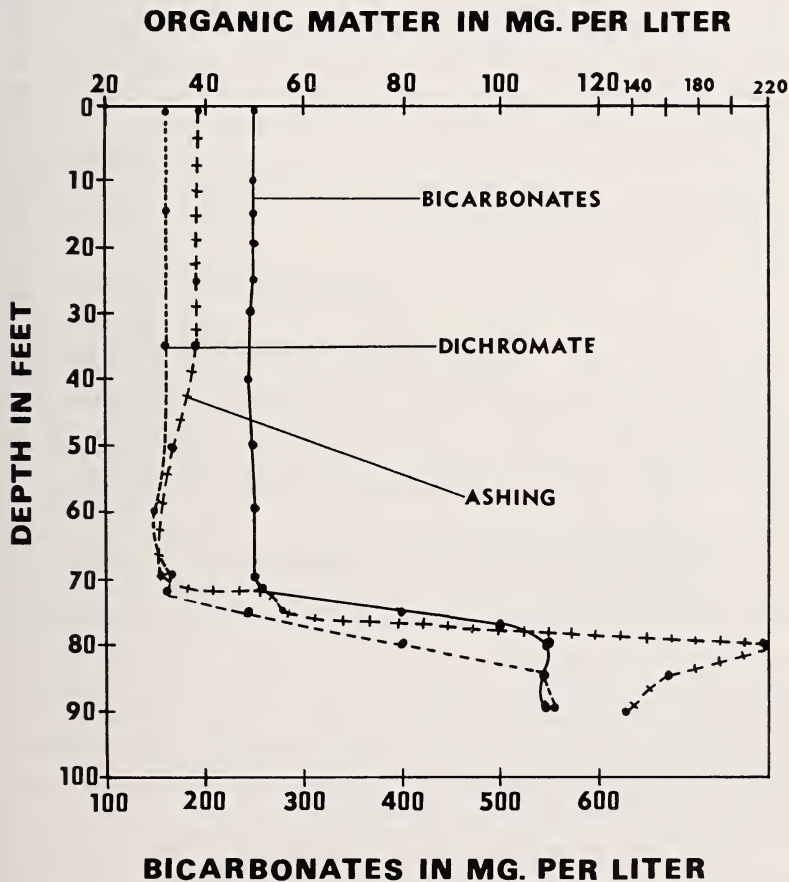


Fig. 2. Vertical distribution of total organic matter in Deep Lake. All samples were collected on March 30, 1968, with the organic matter being analyzed by the dichromate and ashing methods.

per liter at a depth of 85 feet. Below 75 feet there is a great increase in various inorganic substances, such as dissolved gases, chlorides, and bicarbonates. Fig. 2 also shows the results of a comparison of the dichromate and ashing methods in determining total organic matter. The difference in the results obtained by the two methods increases significantly below 75 feet. The largest measured quantity of organic matter using the ashing method was 220 mg per liter at a depth of 85 feet. A dichromate analysis at the same depth showed 110.5 mg per liter of organic matter. Fig. 2 also shows an increase in bicarbonates below 75 feet, with the maximum amount at a depth of 85 feet. The increase in inorganic matter below 75 feet is probably the reason for the increasing disparity between results obtained by the ashing and dichromate methods.

Because of the large quantities of organic matter found below 75 feet, the sample size was reduced from 100-50 ml and the volume of dichromate increased from 5-10 ml.

DISSOLVED AND SUSPENDED MATTER

Water samples were obtained from the Coral Gables Canal (Station 13) over a period of about a month and analyzed to determine the relationship between the amount of suspended and dissolved organic matter. During this period the nature of the canal changed from a running water environment (July 21) because of heavy rains, to virtually that of a pond (August 9), because of low water and the impedance of a salinity dam. There was a reduction in the amount of suspended organic matter from July 21 through the 24 (Fig. 3), probably caused by the decrease in allochthonous material entering the canal when the rains ceased. A plankton pulse of major proportions occurred during the interval and was at its height on August 9. This again caused an increase in suspended organic matter. By August 16 the plankton pulse had ceased and most organisms were in various stages of decay which reduced the amount of suspended matter but tremendously increased the dissolved organic material.

Fig. 3 also shows the amounts of organic matter in the raw water and the amounts which were removed by, and passed through, the plankton centrifuge, Whatman #50 filter paper, and various sizes of milipore filters for each of the four samples pro-

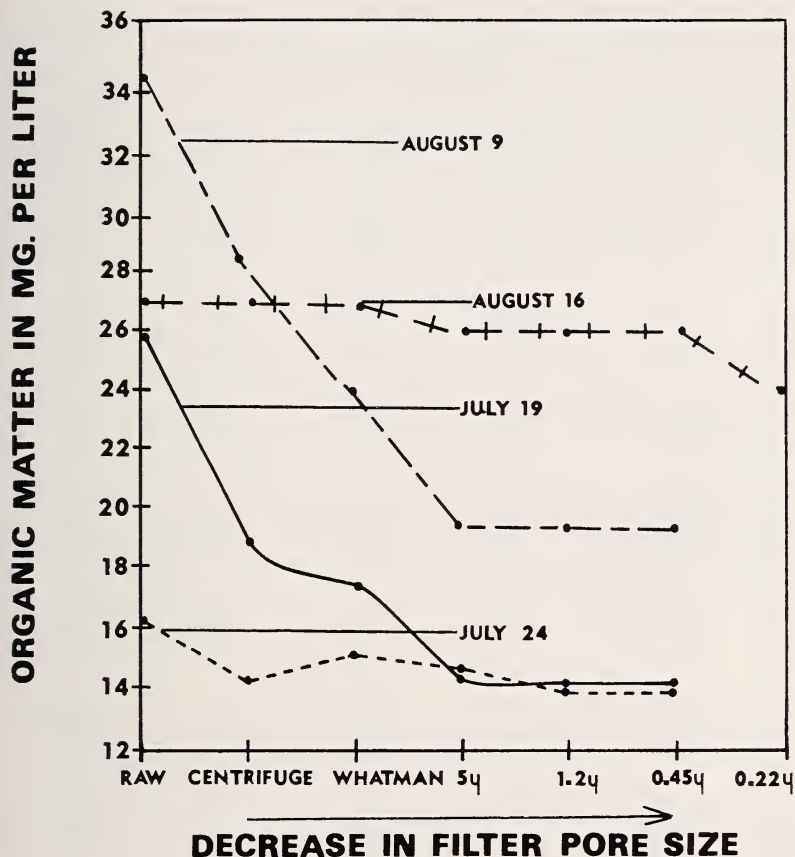


Fig. 3. Comparison of the quantity and the particle size of organic matter in the Coral Gables Canal.

cessed. Of the total organic matter present during this interval the suspended component varied from 1.0-16.6 mg per liter (3.7-48.3 per cent) and dissolved material ranged from 13.9-26.0 mg per liter (51.7-96.3 per cent). It is apparent that even during the heavy plankton pulse the amount of dissolved organic matter, which varied greatly during this short period of time, exceeded one-half of the total.

Measurements of the amounts of suspended and dissolved organic matter in surface waters of 10 of our sampling stations are shown in Table 3. The variability of the total organic content,

TABLE 3

Comparison of suspended and dissolved organic matter*

Station & Date 1968	Sample type	Mean O.C. mg per 100 ml.	Standard deviation	Coefficient variation	Organic matter mg per liter
13 6/28	whole water	4.91	0.090	1.84%	34.4
	filtrate	3.52	0.000	0.00%	17.6
14 7/28	whole water	15.54	0.090	0.55%	108.8
	filtrate	14.10	0.132	0.88%	98.7
15 8/17	whole water	0.87	0.000	0.00%	6.1
	filtrate	0.70	0.040	6.06%	4.9
16 8/10	whole water	7.71	0.000	0.00%	54.0
	filtrate	7.49	0.000	0.00%	52.4
17 8/17	whole water	3.27	0.000	0.00%	22.9
	filtrate	3.23	0.000	0.00%	22.6
18 8/17	whole water	4.55	0.106	2.33%	31.8
	filtrate	4.44	0.000	0.00%	31.0
19 7/27	whole water	5.25	0.000	0.00%	36.8
	filtrate	4.88	0.036	0.74%	34.2
20 8/03	whole water	1.49	0.045	3.04%	10.4
	filtrate	1.39	0.000	0.00%	9.7
21 8/04	whole water	3.04	0.000	0.00%	21.3
	filtrate	3.01	0.000	0.00%	21.1
22 8/10	whole water	3.88	0.000	0.00%	27.2
	filtrate	3.74	0.000	0.00%	26.2

*The results are the means of three 100 ml samples. Filtrate is the material which passed through a 0.45 μ milipore filter.

which ranged from 6.1-108.8 mg per liter, is also reflected in the amounts of dissolved organic material present which ranged from 4.9-98.7 mg per liter. With the exception of the Coral Gables Canal (Station 13) where the dissolved material constituted only 51.2 per cent of the total organic matter on June 28, and 51.7 per cent on August 9 (Fig. 3), the water at the other nine stations had no less than 80.3 per cent of the organic material in the dissolved state. At most stations the dissolved component was in excess of 90.7 per cent with five of the localities having a dissolved organic content ranging from 96.3-99.1 per cent.

These results strongly indicate that usually far less than one-half of the total organic matter in the waters of southern Florida is composed of plankton and larger units of particulate organic debris, and that most of it occurs in a particle size which we consider to be in the dissolved state.

The dichromate method of organic analysis has demonstrated procedural simplicity, very slight variability in replicate sampling, and the capacity to measure with accuracy small differences in these samples.

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